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(54) Bookbinding applications utilizing warm melt polyurethanes

(57) Reactive hot melt polyurethane adhesives are useful for use in the graphic arts area, and in particular, for bookbinding applications such as casemaking, casing-in, gluing-off or thread-securing, facing, slip cases, lining-up, lightbacking, and bonding sides and joints; and for puzzle and gameboard lamination.

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## Description

### Field of the Invention

This invention relates to a method of using a reactive hot melt polyurethane adhesive for graphic art applications, and in particular to a method utilizing a reactive hot melt polyurethane adhesive for bookbinding applications such as casemaking, casing-in, and for gluing-off or thread-securing, facing, slip cases, lining-up, light-backing, and bonding sides and joints, and for puzzle and gameboard lamination.

### Background of the Invention

Adhesives are used for a wide variety of applications in the graphic arts industry such as for bookbinding, and for puzzle and gameboard laminations. In the bookbinding area, one such application is casemaking which refers to the method by which a case or cover for a hard bound book is formed. In this process, the material that forms the outer covering of a book is bonded by the use of adhesives to binder boards, which are usually chipboard, to form the actual "hard" covers of books. The material used for the outer covering may include cloth, paper, leather, vinyl, polyethylene and composite materials such as paper or cloth laminated to polyethylene, polyester or "mylar", and polypropylene. Many other materials are also useful for making book covers, and the list is not limited to those materials mentioned here.

The covering material, which is either in pre-cut form or in continuous web form depending on the type of application equipment used, is passed along a conveyor during which time binder boards, which are usually pre-cut, are mated onto the adhesive coated covering material. If the binder boards are pre-cut in two pieces, then a center strip is usually laid down where the backbone of the book is formed. If the binder boards are pre-cut in one large piece, then two cuts will be made where the backbone of the book is formed. If the covering material is not pre-cut, it will be cut at this point so that it extends up to about 1 inch beyond the perimeter of the binder board. The surplus covering material is then folded over onto the binder board in a two step process known as "turning in" in which either the sides are folded in first and the ends are folded in second resulting in an overlap of the ends over the sides, or the ends are folded in first and the sides are folded in second. These are also called "turn-ins."

The type of adhesive most often used for this application is referred to as "animal glue," although water based emulsions are also used. Animal glue is an amorphous organic colloid derived from animal protein and extended with various plasticizers including water in amounts of between 40% and 50% by weight. Animal glue is usually applied using a roller which is supplied adhesive from a reservoir heated to between about 60°C and about 85°C. This roller then transfers it to one

or two other rollers which will ultimately come into contact with the covering material. Water based emulsions would be applied in a similar fashion, except the reservoir would not require heat.

"Animal glues" and waterbased emulsions both contain substantial amounts of water. Moisture from the adhesive can migrate into the binding board from the adhesive resulting in warpage of the cover. This migration tendency increases as the amount of water present during the process increases. This has an obviously negative impact on the resultant book.

U.S. Pat. No. 4,944,994 to Flanagan issued July 31, 1990 teaches the use of radial styrene-butadiene block copolymer based hot melt pressure sensitive adhesives and U.S. Pat. No. 4,722,650 to Allen et al. issued Feb. 2, 1988 teaches the use of A-B-A block or A-B-A-B-A-B multiblock styrene-butadiene copolymer based hot melt pressure sensitive adhesives for use as casemaking adhesives for "hard" bound books. Major problems can occur with adhesives of this type when used in the casemaking application. First, these pressure sensitive hot melts contain oil which can cause staining and "strike-through" of the cover material especially if the cover material has a natural finish which means the material is of a more porous nature. Staining refers to the oil leaching from the hot melt whereas strike-through refers to the adhesive itself penetrating through the material.

The second problem occurs during what is called "hot stamping" or embossing of the cover. Hot melt adhesives of this nature have melting points of about 90°C which are well below "hot stamping" temperatures of typically about 175°C. The temperatures used for hot stamping may be as low as about 120°C, but this is unusual. This can cause the adhesive to vacate the area where the stamping occurs due to the high temperatures used for this process, resulting in voids and causes the cover material to ultimately separate from the binder board.

A third problem occurs due to the lack of heat resistance of these hot melt pressure sensitive adhesives. If a book is exposed to ambient temperatures in the summer, in a car for example, where temperatures can exceed 75°C the turn-ins may begin to delaminate.

Also, casemaking is typically accomplished through the use of "animal glues" which require application temperatures of about 60°C. The equipment currently used in this industry is capable of application temperatures of no greater than about 130°C. Although the hot melt adhesives of the type taught in Flanagan have melting temperatures of about 90°C, the viscosities are too high at this temperature to be used effectively with the application equipment and require temperatures of greater than about 150°C for effective application. This would therefore require equipment modification which could result in higher cost and is therefore disadvantageous to the book binder.

Puzzles and gameboards can be laminated on equipment similar to that used for casemaking and would therefore have similar requirements. Facing or

"lining-out" is one of the lamination processes used for making puzzles and gameboards. This is the process by which the playing surfaces are laminated to the chip-board base.

Casing-in refers to the process by which the book block is bonded to the inside cover of a "hard" bound book, and therefore occurs after the case making process during which the cover, or case, is made. Casing-in is accomplished by coating the outside of the end sheets of the book block with adhesive, and then laminating the end sheets to the inside of the cover of the book, or by coating the inside of the case or cover and then laminating the end sheets of the book block to it.

The commercial adhesives currently used for the casing-in application are also waterbased emulsions. The substantial amount of water present can again have negative consequences for the book. Too much moisture leads to saturation of the paper which further results in cockling or waviness within the first or last twenty pages due to expansion and contraction of the paper as it dries. Moisture travels inward and causes warping of the paper within the book. Migration of moisture into the cover or case can have a similar effect on the cover wherein positive or negative warping occurs which just refers to the direction of the warp either in toward the pages of the book, or outward.

European Pat. Application 0,279,279 published August 24, 1988 teaches the use of styrene-butadiene-styrene block or multiblock copolymer based adhesive containing a tackifying resin, oil, and optionally a wax for use in casing-in operations, and European Pat. Application 0,358,907 published March 21, 1990 teaches the use of a radial styrene-butadiene block copolymer based adhesive containing a tackifying resin and oil for use in casing-in operations. These formulae are hot melt pressure sensitive adhesives and the disadvantage of using such formulae for casing-in is that the oil content leads to staining of the endsheets. Adhesion will also decrease over time as the oil, which makes a major contribution to the level of tack, wicks out of the adhesive, leaving less oil to plasticize the block copolymer and tackifier.

Further disadvantages can result with the handling of hot melt pressure sensitive adhesives like those formulae above. Due to the fact that a pressure sensitive adhesive remains tacky at ambient temperatures, excess adhesive squeezed out beyond the endsheet on to the case during compression will result in the first page of the book adhering to the case of the book, resulting in undesirable fiber tear from the page. Pressure sensitive adhesives also adhere to equipment, clothes, and skin and are difficult to remove.

Books or booklets may be sewn together through the spine in a two thread sewing method, or are side sewn in what is referred to as McCain stitching. "Gluing-off" is the process by which adhesive is either roll coated or extruded onto the spine of the book or booklet immediately prior to application of the case to prevent unraveling of the thread without damaging the book or

booklet. This is also referred to as thread-securing. The adhesive must effectively coat both the thread that sits on top of the spine of the book or booklet, and the thread that is pulled through the perforations of the spine and looped around the upper thread. These adhesives must therefore have good flow characteristics. Passports are nine-page booklets which are sewn together in this fashion, and an adhesive is then used to secure the threads in a process that is referred to as passport thread-securing. Waterbased emulsions are currently used for this process but they set very slowly and require drying.

Other applications where adhesives are used include "lining-up," "lightbacking," and bonding sides or joints. U.S. Pat. No. 4,660,858 to Flanagan et al. issued April 28, 1987 teaches the use of A-B-A block or A-B-A-B multiblock styrene-butadiene copolymer based hot melt pressure sensitive adhesives and EP Pat. App. No. 0,355,468 A1 teaches the use of radial styrene-butadiene block copolymer based hot melt pressure sensitive adhesives for lining-up applications. U.S. Pat. No. 4,712,808 to Bek-Forrest et al. teaches the use of an A-B-A block or A-B-A-B multiblock styrene-butadiene copolymer based hot melt pressure sensitive adhesives for hinge joint applications. The aforementioned disadvantages of using hot melt pressure sensitive adhesives applies here as well. These inventions do not teach how to make and use a reactive hot melt polyurethane adhesive for lining-up, lightbacking, and bonding sides and joints.

Perfect binding, which is also referred to in the trade as one shot bookbinding, is the most common method by which books are bound. This involves stacking the sheets or signatures of the book, holding them in a clamp to form a book block, applying adhesive to the backbone of the bookblock, and then adhering a cover to the backbone of the book block before the adhesive is set. Hot melts are commonly used for perfect binding because the fast rate of set required for this method can be achieved with hot melt adhesives. "Animal glues" and water based adhesives, in contrast, set slowly and are not as commonly used for this application. Although hot melt adhesives based on thermoplastic polymers, such as ethylene vinyl acetate or block copolymers are most commonly used, it has also been taught that reactive hot melt polyurethane adhesives can also be used.

U.S. Pat. No. 4,942,195 to Flanagan et al. issued July 17, 1990 teaches the use of a radial styrene-butadiene block copolymer based hot melt adhesive for use in the binding of books. Binding in this instance appears to encompass one shot or two shot bookbinding. Hot melts are commonly used because of the fast rate of set that can be achieved. Reactive hot melt polyurethane adhesives, in contrast, are not ideally suited for binding because of their slow cure rates.

Articles have been published on the use of hot melt polyurethanes for perfect binding. Two such articles are Bindery Meets Customer Demands with Polyurethane Reactive Adhesive, Adhesives & Sealants Industry and

General Bindery Shifts to PU Reactive Hot Melts. *Adhesives Age*, August, 1994. Although the benefits of using reactive hot melt PU adhesives is expounded upon in these articles, the disadvantages are not discussed. Reactive PU hot melts have slow cure rates. Prior to cure the books cannot be stressed. If movement or shifting should occur, the books would no longer be satisfactory for shipment which often occurs before the adhesive is cured. Quality control tests cannot, therefore, in some circumstances be performed prior to shipment, and there is no guarantee that the books will meet specifications. Rounding is a process wherein a curvature is made on the spine of the book block. This occurs after addition of crash and kraft to reinforce the book block, and prior to casing-in of the book wherein a cover is bonded to the book block. It is important that the adhesives remain flexible enough to allow the curvature to be maintained for the prolonged life of the book. These adhesives also allow rounding of the book block for an extended period after adhesive application. European pat. application 0 361 122 teaches the use of low viscosity reactive polyurethane hot melt adhesives for use in the rounding application.

The above examples illustrate that attempts have been made to replace hot melts with reactive hot melt polyurethanes. However, no attempts or suggestions have been made to replace water based emulsions or animal glues with reactive hot melt polyurethanes.

The present inventors have now surprisingly found that reactive hot melt polyurethanes can successfully replace water based emulsions and animal glues. Reactive hot melt polyurethanes cure slowly and are more ideally suited for those applications where slower setting products such as water based emulsions and animal glues are used. Hot melts, in contrast, set more quickly and replacing them with reactive hot melt polyurethanes is not as successful.

Binding and rounding of books are very different applications from casemaking, casing-in, and gluing-off or thread-securing applications. Although it is known in the art how to make and use reactive hot melt polyurethane adhesives for binding and rounding, it is not known in the art how to make and use reactive hot melt polyurethane adhesives for casemaking, casing-in, gluing-off or thread-securing, lining-up, tight-backing, bonding sides and joints, and laminating puzzles and gameboards because of the disadvantages noted above. It is the object of the present invention to teach how to utilize reactive hot melt polyurethane adhesives for these applications.

#### Summary of the Invention

The present invention discloses the use of reactive hot melt polyurethane adhesives in the graphic arts area to replace waterbased emulsions and "animal glues," such as for various bookbinding applications, and for gameboard and puzzle lamination. Specifically, the present invention discloses a method of using a

reactive hot melt polyurethane adhesive for casemaking comprising the steps of:

- a) applying a reactive hot melt polyurethane adhesive to the book outer covering material;
- b) placing book binder boards onto the outer covering material; and
- c) laminating the outer covering material to the binder boards.

The invention further discloses a method of using a reactive hot melt polyurethane adhesive for casing-in comprising the steps of:

- a) applying reactive hot melt polyurethane adhesive to the end sheets of a book block; and
- b) laminating the end sheets to the inside of the book cover case.

The invention further discloses a method of using a reactive hot melt polyurethane adhesive for gluing-off or thread-securing comprising the steps of:

- a) sewing a book or booklet together through the spine of the book or booklet using thread;
  - b) extruding reactive hot melt polyurethane adhesive onto the spine of the book or booklet substantially covering the threads; and
  - c) applying the book or booklet case to the spine of the book or booklet;
- wherein the reactive hot melt polyurethane adhesive is between the case and the spine of the book or booklet.

The invention further discloses a case or cover for a hard bound book comprising:

- a) an outer covering material;
  - b) a reactive hot melt polyurethane adhesive laminated to the outer covering material; and
  - c) book binder boards wherein the binder boards are bonded to the outer cover material with the reactive hot melt polyurethane adhesive;
- wherein the adhesive comprises at least one polyfunctional isocyanate component and at least one polymeric polyol component.

The invention further discloses a book comprising:

- a) a book block;
  - b) a reactive hot melt polyurethane adhesive applied to the end sheets of the book block; and
  - c) a book cover or case bonded to the endsheets of the book block with the reactive hot melt polyurethane adhesive;
- wherein the adhesive comprises at least one polyfunctional isocyanate component and at least one polymeric polyol component.

The invention further discloses a sewn book or booklet comprising:

- a) threads sewn through the spine of the book or booklet;
  - b) reactive hot melt polyurethane extruded onto the spine; and
  - c) a case bonded to the spine with the reactive hot melt polyurethane adhesive;
- wherein the adhesive comprises at least one polyfunctional isocyanate component and at least one polymeric polyol component.

These hot melts can be applied at temperatures of less than about 130°C, preferably less than about 105°C, and most preferably less than about 100°C, and are particularly well suited for graphic arts applications including the bookbinding applications of casemaking, casing-in, gluing-off or thread-securing, lining-up, tight-backing, and bonding sides and joints; and puzzle and gameboard lamination. The temperature at which the adhesive can be applied is to a great extent controlled by the green strength required for a particular application. The higher the temperature, the higher the green strength. The viscosities of these adhesives are less than about 10,000 cPs at about 130°C, preferably less than about 10,000 at about 105°C, and most preferably less than about 10,000 cPs at 100°C.

One advantage to using a reactive hot melt PUR for some of these applications is that the same equipment may be utilized for applying reactive hot melt polyurethanes as for "animal glues" with the exception that some cartridge heaters emersed in the hot melt may be required. By using a reactive hot melt PUR, the disadvantages experienced with the high moisture content of the animal glues may be avoided, rates of cure are faster, and adhesion is increased. Replacing water-based emulsions with reactive hot melt PURs also relieves the bookbinder of the disadvantages experienced with the high moisture content, increases the cure rate, and increases the adhesion to a variety of substrates.

Surprisingly, reactive hot melt polyurethanes provide better adhesion to difficult substrates than do water based adhesives or animal glues, providing an added advantage. Another advantage is that the green strength can be controlled by using a higher viscosity adhesive and applying it at a higher temperature. This provides for more flexibility than when using a water based adhesive where the temperature of application and therefore the viscosity and the green strength cannot be varied. Less reactive hot melt polyurethane adhesive will also be required because it cures faster when less is used and the aggressive tack therefore increases with the faster cure.

#### Detailed Descriptions

The reactive hot melt polyurethane useful herein

comprises at least one polyurethane prepolymer. Such polyurethane prepolymers are well known to the industry and are generally formed through the reaction of at least one polyol and an isocyanate resulting in an isocyanate capped polyurethane prepolymer composition. The reaction rate may be increased through the use of a catalyst.

The polyols useful herein are those having an average molecular weight of between about 200 and about 10,000. Their most important feature is that they contain hydroxyl groups or active hydrogen. There are numerous patents and publications teaching the production of polyurethanes such as U.S. Pat. No. 4,808,255 to Markevka et al. issued Feb. 28, 1989 teaching the use of polyester polyols, U.S. Pat. No. 4,820,368 to Markevka et al. teaching the use of polyether polyols, U.S. Pat. 4,775,719 to Markevka et al. issued Oct. 4, 1988 teaching the use of polyhydroxy polyols; and U.S. Pat. No. 5,441,808 to Anderson et al. issued Aug. 15, 1995 teaching the use of a polyester polyether copolymers. One of skill in the art would be familiar with the different methods used to manufacture polyurethane prepolymers.

Examples of polyols useful herein are Voranol® 220-110 N and Voranol® 220-056, polyether polyols available from Dow Chemical Co. located in Midland, MI; Rucolflex® S-107-55 and Dynacoll® 7210, 7250, 7110, and 7111, amorphous polyester polyols available from RUCO Polymer Corp. located in Hicksville, NY and Huls America in Piscataway, NJ respectively; Rucolflex® S-105-36 and Dynacoll® 7340 crystalline polyester polyol available from RUCO Polymer and from Huls America respectively.

Isocyanate compounds useful herein are typically monomeric small molecules having 2 or more -NCO groups. Isocyanate compounds useful for forming the prepolymer include organic, aliphatic, and aromatic isocyanate compounds having an isocyanate functionality of about 2 or more. The isocyanate compounds can have from 1 to 10 aliphatic or aromatic groups substituted by the isocyanate group. The isocyanate compounds can also contain other substituents which do not substantially adversely affect the viscosity of the isocyanate terminated prepolymers, the adhesive properties of the bond line, or the reactivity of the -NCO groups during the formation of the prepolymer. The isocyanate compound can also comprise mixtures of both aromatic and aliphatic isocyanates and isocyanate compounds having both aliphatic and aromatic character.

Typical aromatic isocyanate compounds include diphenylmethane diisocyanate compounds (MDI) including its isomer, carbodiimide modified MDI, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, oligomeric phenyl methylene isocyanates; toluene diisocyanate compounds (TDI) including isomers thereof, tetramethylxylene diisocyanate (TMXDI), isomers of naphthylene diisocyanate, isomers of triphenylmethane triisocyanate, and mixtures thereof. Aliphatic di, tri, and polyisocyanates are also useful

including, for example, isophorone diisocyanate, hydrogenated aromatic diisocyanates, aliphatic polyisocyanate, cycloaliphatic polyisocyanates, and others.

Examples of isocyanate compounds useful herein may include Rubinate<sup>®</sup> 44 manufactured by ICI Polyurethanes Group located in West Deptford, NJ.

The NCO-terminated polyurethane prepolymer is prepared by reacting a stoichiometric excess of diisocyanate with the polyol components. The reactants are in such proportions that the resulting percent isocyanate is in a range from about 1.0% by weight to about 5.0% by weight, and preferably from about 2.0% by weight to about 4.0% by weight based on 100 parts total prepolymer solids. The prepolymer is processed at temperatures in a range from about 70°C to about 110°C, and preferably from about 80°C to about 95°C.

Optionally, catalysts may be utilized to improve curing speed without adversely affecting other physical properties such as green strength or thermal stability. European Pat. Applications 0,492,824,A2 published Jan. 7, 1992, 0,455,400,A2 published June 11, 1991 and 0,668,302,A1 published Aug. 23, 1995 teach the use of 4,4'-(oxydi-2,1-ethanediy)bis-morpholine for use in catalyzing polyurethane reactions. This catalyst is otherwise known as DMDEE and is available under the tradename of Thencat<sup>®</sup> from Texaco Chemical Co. U-Cat 2041, di(2,6-dimethylmorpholinoethyl)ether, is available from Sanapuro Co. and Texacat DMDEE, 2,2-dimorpholinoethyl ether, is available from Texaco Chemical Co. Other catalysts such as ethylene diamine and organo tin and bismuth catalysts such as dibutyl tin dilaurate are not as advantageous.

For more on polyurethane prepolymer synthesis, see Polyurethane Handbook, Gunter Certei, Hanser Publishers, 1985.

Numerous additives can be used to modify such characteristics of polyurethane prepolymers as Tg, viscosity, bonding performance, flexibility, tack, and green strength to name only a few. Such additives may include tackifying resins such as those taught in U.S. Pat. Nos. 4,775,719, 4,820,368, and U.S. Pat. No. 4,808,255 to Markevka et al.; thermoplastic polymers such as those taught in U.S. Pat. No. 4,820,368 to Markevka et al. issued April 11, 1989; polyethylene vinyl monomers such as those taught in U.S. Pat. No. 4,775,719 to Markevka et al. issued Oct. 4, 1988; thermoplastic vinyl polymers such as those taught in U.S. Pat. No. 4,808,255 to Markevka et al. issued Feb. 28, 1989; ethylene vinyl acetate polymers taught in U.S. Pat. No. 4,891,269; ethylenically unsaturated monomers taught in U.S. Pat. No. 5,018,337 issued April 4, 1989; acrylic or methacrylic resins taught in EP 0,246,473 issued Oct. 29, 1988; aromatic oils as taught in JP 61,115,997 issued June 3, 1986 to mention only some.

The adhesives of the present invention are ideally suited for casemaking, puzzle and game board lamination, casing-in, gluing-off or thread-securing, lining-up, tightbacking, and bonding sides or joints.

Casemaking is accomplished using various types

of equipment including, but not limited to, the DA-Chronos casemaker and DA-Strato casemaker manufactured by Kolbus in Rehden, Germany; Model RFC-101 roll fed casemaker manufactured by Crathern Engineering Co. in Contooscook, New Hampshire; BDM 10, 20, 25, and 30 model casemakers made by Hörauf in Donzdorf, Germany; DM 300 casemaker made by Stahl GmbH & Co. in Ludwigsburg-Neckarweihingen, Germany; and Sheridan roll-fed casemakers. Dexter casemakers and Smyth casemakers are in existence but are no longer manufactured. This equipment typically uses a one or two wheel glue pot application in which one wheel may apply the adhesive or transfer the adhesive to another wheel which then applies the adhesive to the cover material and then applies the binder board to the coated cover material. As mentioned before, casemaking is most often accomplished with the use of "animal glues" which are currently applied at about 60°C although the equipment is capable of maintaining adhesive temperatures no greater than about 120°C. The reactive hot melt polyurethane adhesives of the invention could be applied using this equipment. This is advantageous as compared to using other hot melt systems because they typically require much higher temperatures for application and it would therefore require equipment modification resulting in high costs.

Puzzles and gameboards can be laminated utilizing the same or similar equipment to that of casemaking. Crathern Spotters, made by Crathern Engineering Co., are used for this process. Animal glues are generally used for this application.

Applying reactive hot melt polyurethane adhesives for casing-in may be accomplished in a way similarly to that in which water based emulsions are currently applied which is through the use of a roller or series of rollers except that a heated reservoir would be required where water based emulsions are currently used. Typical application equipment for casing-in using water based emulsions are KE and EMP, Compact 2000, and 40, 70 and 100 models from Kolbus which apply adhesives to the endsheets. Lego and Delfores manufacture equipment that applies the adhesive to the cover material first but these are the exceptions to the rule.

Gluing-off or thread-securing is accomplished using an extrusion system where a heated glue pot is utilized.

Tightbacking, lining-up and side or joint glue applications are all accomplished using such equipment as the Compact 2000 model from Kolbus; equipment from Stahl; and equipment from Freccia; and Sheridan round backers are used for lining-up. These applications currently use conventional hot melt adhesives such as ethylene vinyl acetate based products or thermoplastic block copolymer based pressure sensitive adhesives. This equipment would therefore not require modification to encompass the use of a reactive hot melt polyurethane.

Typically, reactive hot melt polyurethane adhesives are applied at temperatures of less than about 130°C.

The adhesives of the present invention may be applied at temperatures of less than about 130°C, preferably less than about 105°C, and most preferably less than about 100°C. The viscosities are less than about 10,000 cPs at about 130°C, preferably less than about 10,000 cPs at about 105°C, and most preferably less than about 10,000 cPs at about 100°C. This will allow a book binder to use reactive hot melt polyurethane adhesives where "animal glues" are currently used, without equipment modification. Crosslinkable Warm-Melts, Dr. Peter Merz, presented to the Paint Research Association, International Centre for Coatings Technology at the *Advances in Adhesives & Sealants Technology Conference*, discussed the use of warm-melt polyurethanes. Warm-melt polyurethanes are a subclass of the broad class of reactive hot melt polyurethanes but are applied at lower temperatures.

Application equipment can also be specifically developed for the application of reactive warm-melt polyurethane adhesives. Drum or pail unloaders and other closed application systems would protect the adhesive from ambient humidity and would be ideally suited for applying reactive warm-melt polyurethanes.

Application equipment can also be specifically developed for the application of reactive warm-melt polyurethane adhesives. Drum or pail unloaders and other closed application systems would protect the adhesive from ambient humidity and would be ideally suited for applying reactive warm-melt polyurethanes.

The following non-limiting examples further illustrate this invention.

## EXAMPLES

### Example 1

To a clean and dry reactor, add 228 parts of Rucolix® S-107-55, 342 parts of a pre-melt of Rucolix® S-105-36 and 228 parts of Voranol® 220-110n and mix at about 55°C. Add 202 parts of Rubinate® 44 and maintain the reaction between about 80°C and about 95°C for about 3 hours. Dissolve about 0.3 parts of Jaffcat® DMDEE into the prepolymer at a temperature of between about 55°C and about 75°C.

The resultant adhesive is characterized by a viscosity of about 25,000 cPs at about 60°C, about 10,000 cPs at about 75°C, and about 5,000 cPs at about 90°C.

The resultant adhesive was further tested by applying adhesive to the end sheets of a book block by coating the end sheets with the adhesive and mating a cover or case to the end sheets therefore simulating a casing-in operation. The adhesive showed full fiber tearing bonds.

### Example 2

To a clean and dry reactor, add 282 parts of Rucolix® S-105-22, 116 parts of Dynacoli® 7240, 88 parts of Dynacoli® 7111, 103 parts of Dynacoli® 7210,

205 parts of Voranol® 220-110n, and 30 parts of Nirez® 2019 and mix at about 120°C for about 30 minutes until a homogeneous polyol mixture is obtained. At a temperature of about 85°C, add 686 parts of Rubinate® 44 and maintain the reaction between about 80°C and about 95°C for about 3 hours.

The resultant adhesive was used in a laboratory simulation of casemaking. The adhesive was first applied to a vinyl cover material and the substrate was bonded to a chipboard binder board in a two step turning-in process in which the sides of the cover material are folded in first and the ends folded in last. The adhesive showed 100% fiber tear. This process was then repeated using a glossy paper cover material and Napura® which is a vinyl type material and the adhesive again showed 100% fiber tear.

### Example 3

The adhesive of Example 1 was tested for performance for gluing-off. A nine-page passport booklet was used and adhesive was applied at a temperature of about 99°C by extruding it onto the threads after the booklet was sewn together through the spine. The adhesive firmly held the threads in place.

## Claims

### 1. A case or cover for a hard bound book, comprising:

- a) an outer covering material;
  - b) a reactive hot melt polyurethane adhesive laminated to the outer covering material; and
  - c) book binder boards;
- wherein the binder boards are bonded to the outer covering material with said reactive hot melt adhesive comprising at least one polyfunctional isocyanate component and at least one polymeric polyol component.

### 2. A book, comprising:

- a) a book block or booklet having a spine;
  - b) a reactive hot melt polyurethane adhesive applied to said end sheets of said book block; and
  - c) a book cover case bonded to said endsheets of said book block with said adhesive;
- wherein said reactive hot melt adhesive comprises at least one polyfunctional isocyanate component and at least one polymeric polyol component.

### 3. A sewn book or booklet, comprising:

- a) a book block or booklet having a spine;
- b) means for binding sewn through said spine;
- c) a reactive hot melt polyurethane adhesive applied to said spine; and

d) a case bonded to said spine with said reactive hot melt polyurethane adhesive;  
wherein the reactive hot melt adhesive comprises at least one polyfunctional isocyanate component and at least one polymeric polyol component.

4. The adhesive of Claim 1, 2 or 3 wherein the application temperature of said adhesive is from about 60° C to about 130° C, or from about 65° C to about 85° C, or from about 80° C to about 100° C.

5. The adhesive of Claim 1, 2 or 3 wherein the viscosity of said adhesive is less than about 10,000 cPs at 100° C, or less than about 10,000 cPs at 85° C.

6. A method of making the case or cover of Claim 1 comprising the steps of:

- a) applying reactive hot melt polyurethane adhesive to the book outer covering material;
- b) placing book binder boards on the book outer covering material; and
- c) laminating the outer covering material to the binder boards.

7. A method of making the book of Claim 2 comprising the steps of:

- a) applying reactive hot melt polyurethane adhesive to the end sheets of a book block; and
- b) laminating the end sheets to the inside of the book cover case.

8. A method of making the book or booklet of Claim 3 comprising the steps of:

- a) sewing a book or booklet together through the spine of the book or booklet;
- b) extruding reactive hot melt polyurethane adhesive on to the spine of the book or booklet, substantially covering the sewn portion; and
- c) applying the book or booklet case to the spine of the book or booklet.

9. The method of Claim 6 wherein the outer covering material is supplied in precut form or selected from the group in continuous web form.

10. The method of Claim 6, 7 or 8 wherein the reactive hot melt polyurethane adhesive is applied by a method selected from the group consisting of heated rollers, in bead form using nozzles and using a spray or spiral filament application.

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(54) **Bookbinding applications utilizing warm melt polyurethanes**

(57) Reactive hot melt polyurethane adhesives are useful for use in the graphic arts area, and in particular, for bookbinding applications such as casemaking, casing-in, gluing-off or thread-securing, facing, slip cases, lining-up, tightbacking, and bonding sides and joints; and for puzzle and gameboard lamination.

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## EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO 94 05738 A (FULLER LICENSING AND FINANCING) 17 March 1994 * page 9, line 25 - line 26 *	1-3	B42D3/00 B42C9/00
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
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The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		26 May 1998	Evans, A
CATEGORY OF CITED DOCUMENTS			
X particularly relevant if taken alone Y particularly relevant if combined with another document of the same category A technological background O non-written disclosure P intermediate document		T theory or principle underlying the invention E earlier patent document, but published on, or after the filing date D document cited in the application I document cited for other reasons S member of the same patent family, corresponding document	

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